

UDC 666.5.015:66.046.52

THE PROCESS OF PORCELAIN FORMATION IN THE PRESENCE OF ADDITIVES (A REVIEW)

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Translated from *Steklo i Keramika*, No. 2, pp. 19–24, February, 1998.

The nature, amount and composition of the introduced additives are shown to affect the process of structure formation in porcelain in several stages. The additives are classified and the mechanism of their action is described.

It is known that the introduction of various additives in the composition of the porcelain mixture is an efficient means of acting on the structure and hence on the properties of porcelain.

In accordance with the mechanism of action of the additives on the process of structure formation in porcelain, the additives are divided into four classes and then differentiated into groups. The first class comprises additives that regulate the coagulation-thixotropic structure of the porcelain suspension and its transition to a condensation structure (electrolytes, surface-active substances, etc.). The second class consists of additives that intensify the sintering process, i.e., accelerate the transformation from a condensation structure to a crystallization and crystallization-pseudocoagulation structure. The third class comprises additives that intensify the process of crystallization of new formations. The fourth class comprises additives virtually insoluble in the molten glass phase which play the role of a source for creating the crystalline phase and improving the quality of the porcelain, including its light-scattering action (zircon, corundum and the like). As a rule, the latter possess a higher refractive index than mullite, quartz and the glass phase, which increases the light scattering capacity of the roasted material.

Depending on the composition, all of the additives are classified as individual and complex. Complex additives are treated as a combination of individual additives.

One and the same additive can be placed in different classes in accordance with its effect on the mechanism of interaction of the initial components in different periods of structure formation. However, a study of its action on the stages of structure formation makes it possible to determine

the predominance of this or that mechanism and choose the most effective composition.

The chemical reactions, physicochemical processes, and structural transformations that occur in a polydisperse mixture (porcelain batch) in the conditions of its preparation and heat treatment act integrally on the phase composition of the mixture and on the properties of the material. In this connection, we considered it expedient to analyze the dependences in the system "composition – structure – property" with the aim of determining the possible regions of existence of structures and describing the processes and mechanisms of the action of mineralizing additives.

The first period consists in the formation of a coagulation-thixotropic structure (CTS) of the porcelain mixture and the transition to a condensation structure. The coagulation structure of a plastic ceramic mixture plays the role of a matrix that serves as the basis for the subsequent types of structure. The temperature range of the existence of the CTS is rather limited (the interval of the first endothermic effect from room temperature to 100–130°C). After the hydrate shells of the clay minerals are removed, coagulation contacts are transformed into point contacts. Some additives, in particular, porcelain scrap, alumina, and fired kaolin, virtually do not interact with the components of the porcelain suspension and therefore do not affect the CTS; on the contrary, soluble additives are quite active. These can be classified as mineral (electrolytes) and organic surface-active substances, i.e., flocculants and deflocculants.

It was established in [1, 2] that the highest decrease in the temperature of the beginning of sintering of porcelain with a minimum content of an additive is attained with the introduction of readily soluble salts. When analyzing the action of insoluble mineral additives, we should take into account the mineral form (the grindability, the capacity for mechanical activation with the other components of the mixture, etc.), the

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initial coarseness of the particles, the degree of uniformity of their distribution over the volume of the mixture [3, 4].

Mineral additives in the form of electrolytes dissolve in the dispersion medium and can exert a peptizing action (for example, borate chalk) or a coagulating action (brucite, magnesite) on the porcelain suspension [2]. In accordance with the Schulze-Hardy rule [5], the coagulation effect of the electrolyte depends on the valence of the ion and its concentration; the higher the valence, the lower the content of the additive. Peptization obeys the opposite rule and therefore even slight dissolution of a calcium-magnesium-containing additive in the dispersion medium promotes coagulation of the porcelain suspension, whereas the introduction of borate chalk containing a sodium salt impurity causes its peptization.

The action of organic additives on the CTS can be illustrated by two examples.

With the introduction of polyacrylamide in the composition of a kaolin suspension, the mean size of the kaolinite aggregates increases and the exchange capacity of the cations decreases.

The polyacrylamide polynomial intensifies the process of aggregation of particles of the disperse phase due to the formation of linear bridges connecting several particles simultaneously; the rest of the chain enters the region of an elevated concentration of cations in the diffusion layer around the particles and neutralizes them [6].

An example of the opposite action is the introduction of a liquid *B. mucilaginosus* bacteria culture in the composition of the porcelain mixture [7]. As a result of the activity of the bacteria, the dispersion medium is enriched with exopolysaccharides, i.e., surface-active substances that promote deflocculation of the clay particles. This process increases the number of particles per unit of volume of the ceramic suspension and hence increases the number of contacts whose strength is, however, lower than in a suspension containing no additive. In contrast to mineral electrolytes, which block the adsorption centers on the surface of the dispersed components, the molecules of organic SAS are adsorbed on cleavages and edges of kaolinite particles, neutralizing their positive charge. The presence of such a charge in the system causes the formation of spatial coagulation structures of the plane-edge type. This is accompanied by breaking of some hydrogen bonds in the aggregates, and their sizes decrease. One of the consequences of neutralization of positive charges is an increase in the total negative charge of the particles, an increase in their stability, and slowing of thixotropic reduction.

In this connection, uniform distribution of the additive over the volume of the porcelain suspension becomes a very important condition for coagulation-thixotropic structure formation. The introduction of soluble additives promotes a change in the number and type of coagulation contacts between particles of the disperse phase.

When the porcelain mixture is dried, the hydrate shells of the clay particles are removed; the coagulation contacts transform into condensation ones up to the appearance of condens-

sation-crystallization contacts; the substance is transferred through the vapor phase and precipitates on particles of the disperse phase predominantly of clay components in the form of amorphous and weakly crystallized oxide and hydroxide films which densely bind separate particles into aggregates.

The second period consists in crystallization structure formation of the solid disperse phase of the porcelain mixture in the temperature range of 400 – 800°C. The presence of additives in the mixture in this temperature range causes differences in the structural and phase transformations of the components and in the kinetics of the initial sintering state.

As the temperature is increased to a level exceeding that of the existence of condensation structures, the minerals i.e., aluminosilicates (kaolinite, muscovite etc.), iron hydroxides (goethite, hydrogoethite), and magnesium hydroxides (brucite) undergo dehydroxylation reactions and decarbonization reactions (siderite, calcite, etc.).

The temperature of the minimum (570 – 600°C) and the width of the interval of the endothermic effect (465 – 730°C) of the porcelain mixture with a mineralizer can remain virtually unchanged. The introduction of other additives into the mixture, for example, brucite, is characterized by a shift in the temperature of the minimum and by widening of the range of the endothermic effect. The shift is caused by the endothermic effect in the 355 – 480°C range due to dehydration of brucite [2].

In all probability, the removal of coordinated OH ions is accompanied by rearrangement of the crystal lattice of the minerals and the formation of intermediate products.

A porcelain mixture containing no additive begins to be compacted at 930 – 950°C. The same process in porcelain mixtures containing a water-soluble additive or brucite is shifted to the region of lower temperatures by 30 – 200°C [2]. Since the driving force of the process of solid phase sintering in porcelain systems of various compositions remains the same (surface energy [8, 9]), the difference in the behavior of mixtures with additives can only be connected with differences in the mechanism of transfer of matter, i.e., evaporation-condensation, surface and bulk diffusion.

The increase in the difference in the chemical potentials at the boundaries of particle-particle and particle-film contacts is the driving force that activates transfer of matter. This determines the leading role of thermal diffusion processes in solid-phase sintering and the formation of crystallization structures.

The free oxides that appear as a result of thermal fracture of the minerals present in the porcelain mixture in the form of films or thermally fractured additives penetrate the lattice of metakaolinite, compensate the excess negative charge, and form an unsteady, intermediate, finely dispersed phase, i.e., a solid solution. This phase is characterized by an active state susceptible to recrystallization, accompanied by the formation of activation centers.

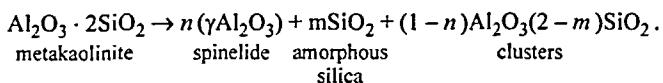
Thus, two groups of additives participate in the process of crystallization structure formation in the solid phase of a

porcelain mixture, namely, the soluble additives that condense on clay particles in drying up to the appearance of condensation-crystallization structures, and mineral additives that break due to dehydration and decarbonization in the 400 – 800°C range. These two groups of additives thermally activate the process of metakaolinite destruction with the formation of intermediate compounds, i.e., activation centers of mullite formation.

The third period consists in crystallization-pseudocoagulation structure formation at a temperature ranging from 800 – 900 to 1100°C. The appearance of an eutectic melt in this temperature range determines the new interphase boundaries of the disperse phase that interacts through the liquid phase, causing the formation of pseudocoagulation contacts. The liquid phase intensifies processes of mass transfer due to diffusion and viscous flow.

Solid-phase reactions continue in the region of crystallization-pseudocoagulation structure formation with the formation of mullite from the products of the decomposition of metakaolinite and inside the amorphized grains of feldspar that still preserve their order. These solid phase reactions have a topochemical nature and are realized in correspondence with the theory of structural inheritance.

According to the data of I. Kh. Moroz [10], the solid-phase reaction of decomposition of metakaolinite causes its amorphization and partial segregation into oxides with an increase in the temperature. However, the process does not end in full segregation of metakaolinite, possibly because of impeded diffusion in the solid state. Therefore, the oxides are accompanied by clusters with a partially ordered structure, i.e.,



The spinelide crystals in the heterogeneous structure of the formed material can act as crystallization centers, i.e., nuclei for the appearance of mullite crystals.

Mullite crystals formed over kaolinite grains have much larger sizes than the particles of the initial kaolinite, but preserve similar orientation and homogeneity. It should be taken into account that the system formed in segregation of metakaolinite into oxides and clusters in the process of transformation of metakaolinite into mullite is characterized by an extremely high specific surface area, which can lead to a heterogeneous formation of crystallization centers. In addition, the size of the growing crystals is limited by the size of the particles of the initial material. In this stage of the firing process diffusion occurs slowly (the case when the reaction system is supersaturated on the substrate).

Consequently, the rate of mullite formation is predominantly determined by the rate of formation of crystallization centers; the latter is proportional to the volume of the spinelide formed in the system. In this connection, a substantial role is played by the appearance of clusters in the processes of structure formation in porcelain. In accordance with

the results in [9], if the size of the formed cluster exceeds a certain critical value, it grows further, but if its size is below the critical value, the cluster dissolves. Mineralizers change the occurrence of the process of crystallization-pseudocoagulation structure formation quite substantially.

First, the mineralizing additive shifts the beginning of the appearance of the melt into the region of lower temperatures due to the formation of eutectics and thus changes the structure and properties of the melt. For example, when the mixture is enriched by a magnesium oxide additive that consists of magnesium and zinc, the temperature of the appearance of the liquid phase decreases by 100 – 120°C and the apparent viscosity decreases too. In addition, the apparent viscosity decreases monotonically with an increase in the temperature up to the beginning of mullite crystallization.

Second, the introduction of metal oxides of the second group (CaO, MgO, ZnO, BaO) shifts the temperature of the maximum of the first exothermic effect by 20 – 70°C and that of the minimum of the temperature dependence of the apparent viscosity by 20 – 50°C [11, 12].

According to modern concepts, the nature of the exothermic effect is connected with crystallization of spinelide and the formation of nuclei of mullite crystals. Small additions of metal oxides act so that magnesium oxide promotes the formation of spinelide; calcium oxide seems to transform the clusters into gelenite, which plays the role of seeds for mullite crystallization. Since the process of mullite crystallization corresponds to the model of nucleation growth, and the addition of calcium and magnesium oxides intensifies segregation, exerting a selective action on metakaolinite, spontaneous nucleation is shifted into the region of lower temperatures. The rate of mullite crystallization increases considerably.

Third, the eutectic melt is characterized by lower viscosity, which activates thermal diffusion processes and increases its dissolving power.

The microstructure of the product of transformation of metakaolinite is characterized by the fact that one of the phases (mullite) is distributed in the form of islands inside the other phase, represented by particles of amorphous silica surrounded by aluminosilicate clusters. With an increase in the temperature, the amorphous silica dissolves in the eutectic melt formed with the participation of the mineralizers, the equilibrium is shifted, and the clusters start to segregate.

Fourth, introduction of additives intensifies the process of compaction of the porcelain mixture due to viscous flow, the appearance of liquid films between the components of the porcelain mixture, activation of thermal diffusion processes between the amorphized grains of feldspar and the products of decomposition of metakaolinite, which serves as the bases for mullite formation in amorphized feldspar grains. Several more consecutive stages of mullite formation can be distinguished, namely, predominant diffusion of cations of alkaline metals from the feldspar skeleton into the acid silicate amorphized product of decomposition of kaolinite; the response

diffusion of Al^{3+} cations into the skeleton; transformation of the orthoclase chain into a sillimanite-mullite one over which a column of $[\text{AlO}_6]$ octahedrons appearing due to the introduced aluminum cations is formed.

It was suggested in [13] that preservation of the general pattern of the arrangement of aluminum-silicon-oxygen tetrahedrons promotes the formation of needle mullite crystals extending in this direction.

Fifth, a magnetically ordered phase is formed simultaneously with the emission of alumina and silica in segregation of metakaolinite at 800 – 900°C; as the temperature exceeds 950°C, the phase decomposes and passes into a paramagnetic state. A minor part of the iron ions enters the structure of mullite ("silicate" iron) because the isomorphic capacity of mullite with respect to iron is inconsiderable, and the major part is emitted in the form of clusters in the heterophase system of the product of heating.

The fourth period consists in crystallization of the new formations from the molten glass phase. This stage corresponds to sintering with the participation of a liquid phase that reacts with the solid phase (at 1100 to 1400°C). The liquid phase is formed due to melting of feldspar and due to dissolution of quartz and decomposition of metakaolinite with the formation of amorphous silica and sericite, which melts incongruently with the formation of mullite, leucite and amorphous silica [14]. The acceleration of melting of the liquid phase is connected with the appearance of eutectics. The action of mineralizers on the process of crystallization of new formations from the liquid phase melt is characterized by a change in the chemical composition and kinetics of the process of the appearance of a glass phase melt with the participation of calcium-magnesium-silicate additives (diopside, tremolite), which melt at a relatively high temperature in contrast to other mineral additives (brucite, chalk, magnesite, etc.).

In addition, the structure formation of porcelain in the solid phase stage occurs with the formation of intermediate phases caused by the high concentration gradient in two touching particles. In accordance with the Ostwald step rule, if a solid solution is formed from a substance in the amorphous state, it has high solubility. In further heating, when the content of the solvent is sufficient, the solid solution can be decomposed and then formed again at a higher temperature. In accordance with Dankov's principle of orientation-ordered correspondences (rule of structural inheritance), which is a modification of Ostwald's rule, this system will again form phases whose structure differs as little as possible from the structure of the initial substance.

In this connection, it is quite natural that the stage of structure formation characterized by the appearance of a considerable amount of aluminosilicate melt occurs with the dissolution of primary mullite, total dissolution of clusters, i.e., products of the decomposition of metakaolinite or their transformation into a crystalline phase, for example, anorthite, and predominant crystallization of new formations from the melt,

i.e., differently shaped mullite crystals (acicular, prismatic, etc.), anorthite, cordierite, and cristobalite-tridymite.

With the use of mineral additives that contain a set of oxides including calcium and magnesium monoxides, the mechanism of diffusion of the oxides of alkaline and alkaline-earth metals into a melt of the vitreous phase of porcelain is quite complex [15, 16].

An electron microscopic analysis confirmed the data of B. G. Varshal [17 – 19] showing that in the formation of the microstructure of the vitreous phase, Ca^{2+} and Mg^{2+} cations migrate into different segregation components. It is possible that this is the reason behind the order of segregation of the new crystalline phases, i.e., anorthite and cordierite.

Anorthite crystals appear in pseudomorphoses on feldspar; K^+ ions are substituted by Ca^{2+} ions with the formation of anorthite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. It is possible that mullite is the first to appear in pseudomorphoses on potassium feldspar and then (with the introduction of Ca^{2+}) anorthite appears over the mullite crystals.

In regions of pseudomorphoses on feldspar where the number of Ca^{2+} ions is insufficient for the formation of anorthite, Ca^{2+} ions are concentrated on the crystal – glass phase boundary. It seems that these regions promote the appearance of liquation drops over the mullite crystals in cooling.

The very phenomenon of phase segregation in porcelain was first established by I. Kh. Moroz, who studied the structure of porcelain with a phosphorus-bearing additive. Addition of the oxide of an alkaline-earth metal is assimilated by the feldspar melt and this seems to affect the structure of the melt and hence the structure of the glass phase, causing the formation of segregation regions in some cases. The special features of the segregation structure depend on the nature of the modifying ion. It is known that segregation of silicate glass intensifies with a decrease in the basicity of the melt. Segregation of an aluminosilicate melt in the formation of porcelain is observed with introduction of Ca^{2+} and Mg^{2+} ions. The concentration of the segregated substance on the surface of mullite crystals indicates the attempt of the system to decrease the internal energy by decreasing the energy of the glass-mullite crystal interface, which should remove some stresses from the interface.

With diffusion of oxides of the elements of the second group into the aluminosilicate melt, the structure of the latter changes, which promotes the formation of cybotaxis groups corresponding to the structure of the lattice of the newly formed phases, i.e., cordierite, anorthite and cristobalite. It should be noted that in the case of the coexistence of more or less polymerized structures, the crystallization process is governed by less polymerized structures more susceptible of crystallization.

The difference in the behavior of aluminosilicate melts with additives of oxides of bivalent metals under a thermal effect is caused by the composition of the coordination polyhedrons and the strength of the chemical bond in the main structural element.

The properties of the melts are primarily determined by the Si – O bond in the Si – O – Si structural unit. The bonding force is measured by the coefficient f_{Si} and the capacity of the Al³⁺ ion for transition from one coordination into another is determined by the Al-to-Si ratio [20]. The feldspar melt is represented by silicon-oxygen radicals continuous in two dimensions and possessing one “weakened vertex;” the calcium-containing melt consists of silicon-oxygen radicals continuous in one dimension and possessing two “weakened vertices;” the magnesium-containing melt consists of discrete twin tetrahedrons with three “weakened vertices” [21].

The microheterogeneous structure of the melt determines the genetic tie between the structural components of each elementary region of the heterophase system and the products of their crystallization.

The structural components of the initial melt should not be mixed fully in the initial melt that forms the glass phase of porcelain with a set of mineralizing additives, because two or more types of crystal form from the melt. The composition of the segregated crystalline phases in cooling of the melt depends considerably on the phase diagram of the system of each elementary region.

For example, with an increase in the content of diopside additive in the batch, the phase composition and structure of the porcelain changes. As the melt is saturated with calcium and magnesium oxides, the primary phase (mullite) begins to crystallize (for a 1 – 5% diopside content), which is followed by crystallization of anorthite. As the content of diopside in the mixture increases, the concentration of CaO in the melt increases, which promotes crystallization of a large amount of anorthite and decreases the content of mullite. The concentration of silicon oxide in the composition of the feldspar melt (a feldspar pseudomorphosis) decreases and the concentration of calcium oxide increases. The content of magnesium and aluminum oxides on the boundary of the fusion zone of quartz sand increases, which causes crystallization of cordierite and a change in the ratio of the crystalline phases, i.e., quartz, mullite, cordierite, and anorthite.

The action of mineralizers, i.e., oxides of alkaline-earth metals, on the structure, properties and composition of the melt forming the glass phase of porcelain causes specific changes in the structural and phase state and the level of the organization of iron compounds, namely, an increase in the content of calcium oxides and especially, of magnesium oxides, causes crushing of the silicon-oxygen skeleton and makes the iron cations together with aluminum cations change from four coordination to six coordination. As a consequence, Fe(III) ions occupy the octahedral vacancies forming iron-oxygen polyhedrons or exchangeable Fe(II) – O – Fe(III) groups. Iron ions in six coordination promote the development of segregation regions in the melt due to the incompatibility of the iron-oxygen octahedrons with the silicon-oxygen skeleton; it seems that in cooling they segregate in the form of a second phase which is paramagnetic at a room temperature because magnesium and especially alumini-

num ions are segregated by the mechanism of heterovalent isomorphism.

In analyzing the data presented above, we can make the following conclusions.

The studies conducted with complex thermographic, x-ray phase, electron microscopic, microscopic x-ray spectral, and other modern physicochemical methods of analysis make it possible to describe quite reliably the mechanism of action of additives on the process of structure formation in porcelain.

It seems expedient to divide the additives used in the porcelain industry into four classes, namely:

additives controlling the coagulation-thixotropic structure of the porcelain mixture;

additives controlling the sintering process in the stage of the occurrence of solid phase reactions;

additives intensifying the process of crystallization of new formations;

additives inert with respect to the dissolving capacity of the aluminosilicate melt that forms the vitreous phase in cooling, which provides for some valuable properties of the material.

The statement that the crystallization process of the phases that constitute the base of the porcelain structure such as mullite, cordierite, and anorthite are intensified considerably by the use of magnesium and calcium monoxide additives is of a great practical importance. The change in the phase composition and structure of the porcelain due to the action of complex additives promotes curing of the material and improves its properties.

The introduction of additives should change the nature of porcelain coloring. For example, the action of magnesium and calcium monoxide additives reduces the redness and yellowness of porcelain due to decomposition of iron-containing complexes (clusters and associates) and their uniform distribution over the bulk of the aluminosilicate matrix in the form of [FeO] polyhedrons and due to the change in the coordination of [FeO₄] iron-oxygen polyhedrons for [FeO₆].

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